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Intramolecular Interaction, Photoisomerization, and Mechanical C−C Bond Dissociation of 1,2-Di(9-anthryl)benzene and Its Photoisomer: A Fundamental Moiety of Anthracene-Based π-Cluster Molecules

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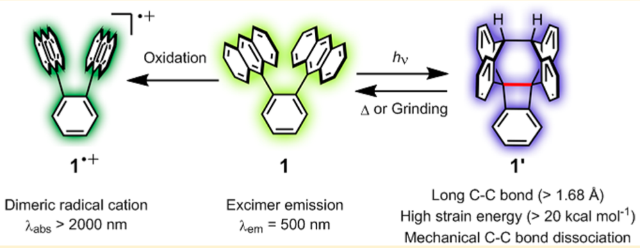
Ⓢ *Supporting Information*

ABSTRACT: We report variable and unique properties of 1,2-di(9-anthryl)benzene **1** as a fundamental moiety of anthracene-based π-cluster molecules. Due to a through-space π-conjugation between anthracene units, excimer emission at room temperature and charge delocalized state in radical cation state of **1** could be observed. Photoirradiation to **1** afforded an intramolecular [4 + 4] cyclized anthracene dimer **1′** having a high strain energy with long C−C bond that exceeded 1.68 Å, resulting in C−C bond dissociation by simple mechanical grinding.



INTRODUCTION

To construct new π-conjugated systems composed of aromatic units, variable concepts such as designing the π-conjugation manner from one- to three dimensions[1] and doping hetero- or metal atom(s) in the π-system[2] have been widely investigated, and their fundamental properties have been evaluated to understand the structure−property relationship and to find good candidates for high-performance organic devices.[3] One of unique π-conjugated systems in our interests is a through-space π-conjugation. [2.2]Paracyclophane is a typical compound showing the through-space π-conjugation because the distance of two benzene rings is shorter than the sum of van der Waals radius of carbon atom (3.40 Å) resulting in overlapping the π-orbitals on their aromatic rings.[4] Therefore, a lot of derivatives have been synthesized and investigated.[5] Inspired from these pioneering works, we designed a new π-system having through-space π-conjugation composed of anthracene units arranged in cyclic or radial manner (Figure 1). Due to the distance between anthracene units at 9, 9′ positions being <3.40 Å, they can show the through-space π-conjugation. These anthracene-clustered molecules, that is, π-cluster system, are interesting in optoelectronics, especially to investigate the electron-transfer process and charge delocalization behavior in excited state or oxidation state.[6] In addition, thanks to employing anthracenes, a photoirradiated structural switching property[7] is anticipated which can be applied for controlling the optoelectronic properties as well as for solar thermal storage using its strain energy.[8]

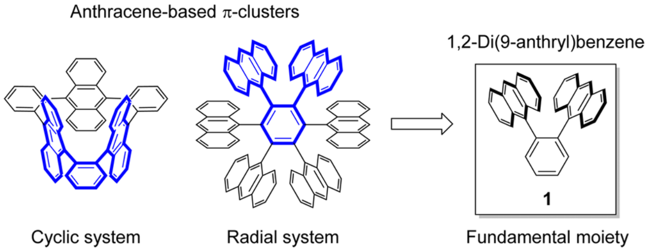


Figure 1. Anthracene-based cyclic and radial π-cluster systems and 1,2-di(9-anthryl)benzene **1** as a substructure of the systems.

To evaluate the through-space π-conjugation and photoisomerization between anthracene units, 1,2-di(9-anthryl)-benzene **1**, which is one of anthracene dimers[9] and the fundamental moiety of anthracene-based cyclic and radial π-cluster, was prepared. Herein, the structure, optoelectronic properties not only in neutral but also in oxidation state, and photoisomerization behavior of **1** as well as the C−C bond dissociation of its photoisomer **1′** are reported.

RESULTS AND DISCUSSION

Although the synthesis of **1** was first achieved by Yamazaki et al. using Suzuki−Miyaura cross coupling, the yield was quite low (4%).[10] We modified the reaction condition, by changing the base and solvent, and the yield could be improved up to 32% yield (Scheme 1).

The structure was confirmed by X-ray crystallographic analysis (Figure 2). To reduce the steric hindrance between anthracene units, anthracenes are not perpendicular to benzene ring, and the torsion angle is 72.3°. Although the distance of C10···C10′ is 6.6617(29) Å, a short C9···C9′ contact of 3.1082(24) Å results in orbital overlapping of anthracene units confirmed by quantum chemical calculations (Figure S5). With the short contact, each frontier orbital (that is, HOMO and

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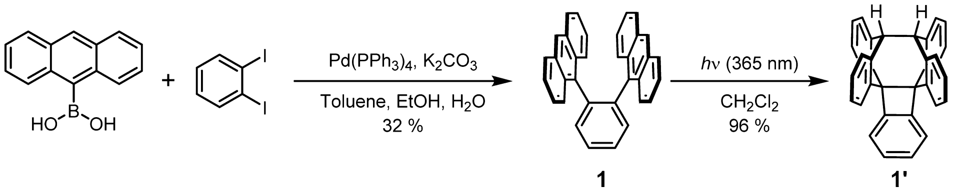
Scheme 1. Synthesis of 1,2-Di(9-anthryl)benzene 1 and Its Photoisomer 1′



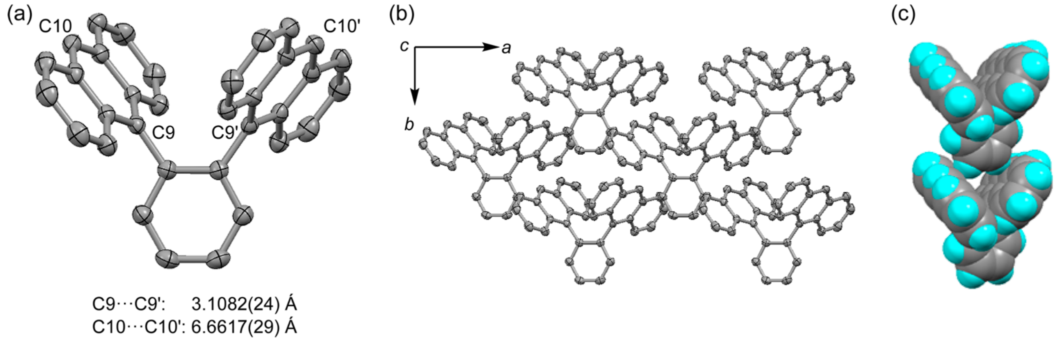


Figure 2. X-ray crystallographic analyses of 1,2-di(9-anthryl)benzene **1**. (a) Front view of **1**. (b) Packing structure of **1**. Protons are omitted for clarity. Displacement of ellipsoids are drawn at the 50% probability level. (c) Dimer structure (CPK model) of **1**.

LUMO) of anthracene splits into destabilized and stabilized molecular orbitals with small energy gap corresponding to HOMO and HOMO−1 ($\Delta E = 0.124$ eV) as well as LUMO+1 and LUMO ($\Delta E = 0.090$ eV) for **1**, respectively. These small energy splittings are attributed to only one side tethering of two anthracenes. In the packing structure, no recrystallized solvents are included, and intermolecular CH−π interaction between central benzene ring and two anthracene units is observed to occupy the space (Figure 2b,c). The C···C distance is 3.645 Å which is less than the sum of van der Waals radii of proton and carbon atoms (Figure S3).

As expected, by photoirradiation (365 nm) of **1** in solution, intramolecular [4 + 4] cyclization to afford **1′** smoothly proceeded quantitatively, and **1′** could be purified by silica gel column chromatography (Scheme 1). Although the reverse photoisomerization from **1′** to **1** using a low-pressure mercury lamp (250 nm) was attempted, only a trace amount of **1** was confirmed by ^{1}H NMR because **1** also absorbs the light at 250 nm and the molar absorption coefficient of **1** is greater than that of **1′**. Fortunately, single crystals suitable for measuring X-ray crystallographic analysis were obtained, and the structure of photoisomer **1′** was unambiguously identified (Figure 3).

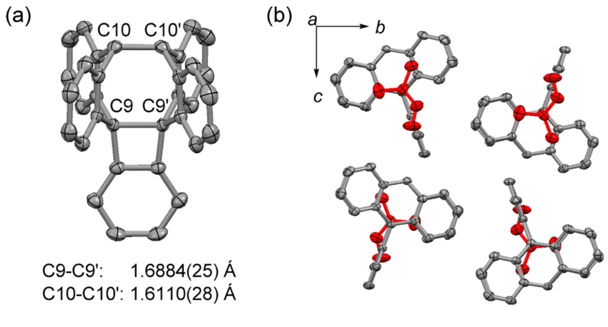


Figure 3. X-ray crystallographic analyses of photoisomer **1′**. (a) Front view. (b) Packing structure of **1′**. DMF is represented as red color. Protons are omitted for clarity. Displacement of ellipsoids are drawn at the 50% probability level.

The bond lengths of C9−C9′ and C10−C10′ in **1′** showed a large difference, and these lengths are 1.6884(25) and 1.6110(28) Å, respectively. Quantum chemical calculations (DFT) could also reproduce these C−C bond lengths (Figure S6). Compared with other reported anthracene photodimer derivatives, the C−C bond length of 1.6884 Å is extremely long[11] due to the four-membered ring strain of benzocyclobutene.[12] However, the C−C bond length is not reaching at 1.700 Å like several hexaphenylethane (HPE) derivatives because, between the C−C bond, not only the small ring strain but also a steric hindrance by bulky substituents are required for exceeding 1.700 Å.[13]

Different from the packing structure of **1**, that of **1′** showed no intrermolecular CH−π interactions like **1**, and the recrystallized solvent (*N*,*N*-dimetylformamide) is included (Figure 3b).

In crystalline state, the photoisomerization from **1** to **1′** was attempted, but no isomerization was confirmed because, in the packing structure as shown in Figure 2b,c, a central benzene unit penetrates the space between anthracene units of neighbor molecule, restricting a molecular dynamics and excimer formation.

UV−vis and fluorescence spectra of **1**, **1′**, and 9-phenylanthracene **2** as a reference are shown in Figure 4. In UV−vis spectra, **1** showed a maximum absorption at 395 nm with a slight bathochromic shift of 10 nm compared with **2** (385 nm). However, in fluorescence spectra of **1**, a broad spectra and yellow emission from 425 to 500 nm with large bathochromic shift of 80 nm compared with **2** (420 nm) was observed, indicating not only an emission from phenylanthracene moiety but also an intramolecular excimer formation between anthracene units. On the contrary, **1′** showed a maximum absorption at 250 nm with small molar adsorption coefficient and no emission due to losing the π-conjugation by dimerization of anthracene units.

In crystalline state, the emission of **1** showed a blue color which is an identical shape with that of **2** because the excimer formation is disturbed by a neighbor molecule (Figure 2b,c). Then, the emission quantum yield of **1** is enhanced from 9% in

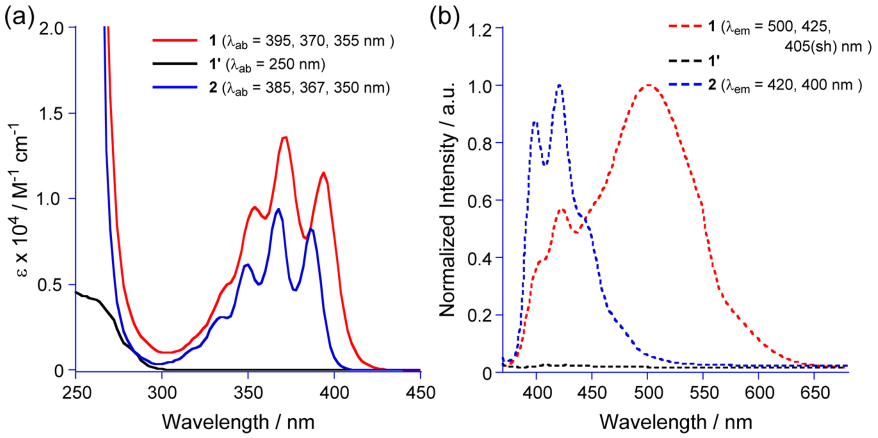


Figure 4. (a) UV−vis spectra of **1**, **1′**, and **2** in CH_2Cl_2. (b) Fluorescence spectra of **1**, **1′**, and **2**. For the normalization of **1′**, the intensity of **1** at 500 nm was used for comparing the ratio of intensities between **1** and **1′**.

solution (CH_2Cl_2) up to 30% in crystalline state (Table 1). Interestingly, by grinding the crystal of **1**, the solid color changed from colorless to pale yellow, and a yellow emission derived from excimer could be observed probably because the grinding induced a deconstruction of the intermolecular interaction (Figures S7 and S8).[14]

Table 1. Quantum Yields of 1 and 2 in Solution and Solid State

1			2	
solution (CH_2Cl_2)	crystal	ground	solution (CH_2Cl_2)	ground
9%	30%	12%	52%	87%

Intramolecular anthracene−anthracene interaction of **1** was also observed in the oxidation state by cyclic voltammetry (CV) (Figure S9). Four oxidation waves (one reversible and three irreversible) at E = +0.76, +1.02, +1.24, and +1.54 V (vs Fc/Fc^+) were confirmed, indicating an one-electron four-step oxidation process, corresponding to radical cation, di(radical cation), dication−radical cation, and dication state, respectively, whereas **2** showed two oxidation waves (one reversible and one irreversible) at E = +0.87 and +1.38 V, corresponding to radical cation and dication state. The first oxidation potential of **1** is lower than that of **2** due to the through-space π-conjugation, and at the first oxidation state, $\mathbf{1}^{\cdot+}$ seems to form a charge delocalization state between anthracene units.[15] Therefore, to evaluate the first oxidation state of **1**, an oxidative UV−vis-NIR titration using $SbCl_5$ was conducted (Figure 5).

By adding the oxidant from 1, 2, 3, 4, and to 5 equiv,[16] a new sharp absorption at 750 nm and a broad absorption centered over 2000 nm are observed. The same titration for **2** was conducted, but the broad absorption was not observed (Figure S11). From TD-DFT calculations, the broad absorption band is assigned as a combination of HOMO−1 → SOMO and SOMO → LUMO transitions (Figure S10), that is, a charge delocalized band. Because two anthracene units are radially arranged and tightly fixed by benzene ring, the stabilization energy of dimeric radical cation seems to be relatively weak compared with a case of face-to-face interaction and, therefore, the charge delocalized band is shown as a highly broadened shape over 2000 nm.[15] In fact, the optimized structure of $\mathbf{1}^{\cdot+}$ in UB3LYP/6-31G** showed that, compared with neutral state of **1**, the distance between anthracene units get shorter to 2.943 Å at C9···C9′, but the distance at C10···C10′ is still far (5.626 Å), constructing the weak dimeric radical cation (Figure S6). The charge delocalization behavior is also observed in ESR measurement. The spectra were shown as multibroadened

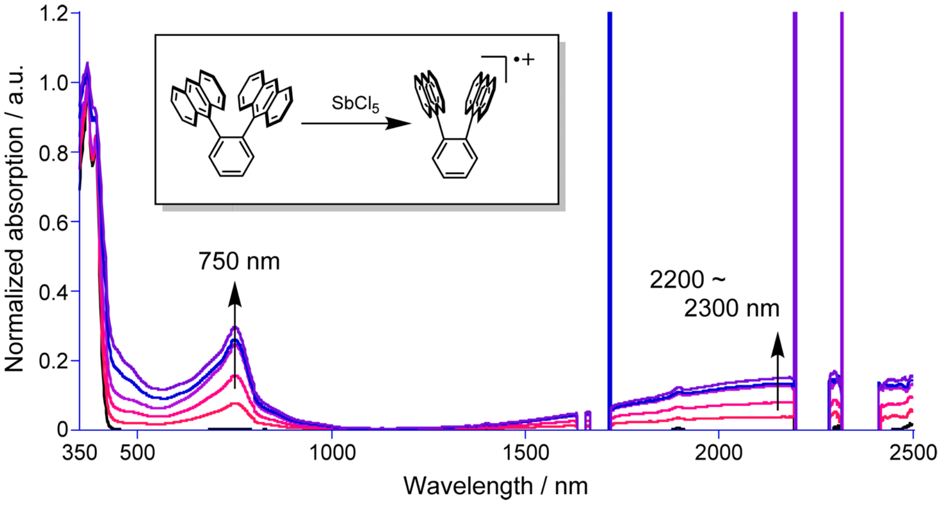


Figure 5. UV−vis-NIR titration of **1** (1.0×10^{-4} M in CH_2Cl_2) with $SbCl_5$ (0−5 equiv).

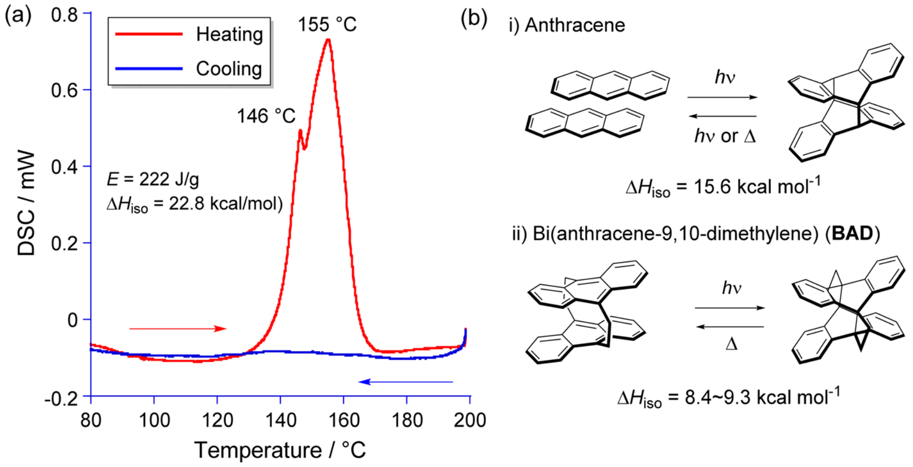
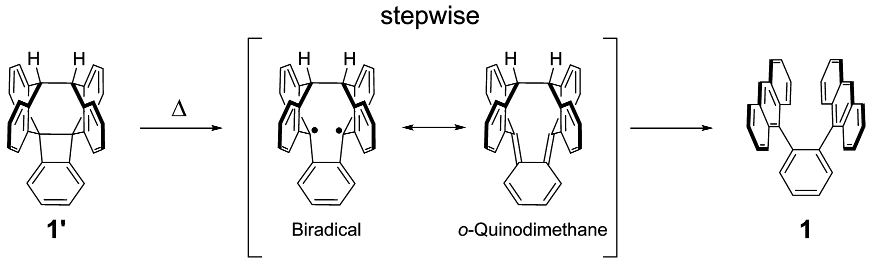


Figure 6. (a) A DSC chart of **1**′ (heating rate: 2 °C/min). (b) The energy differences (ΔH_{iso}) between (i) anthracene and anthracene dimer, and (ii) bi(anthracene-9,10-dimethylene) and its photoisomer.

Scheme 2. Plausible C−C Bond Dissociation Pathways from 1′ to 1



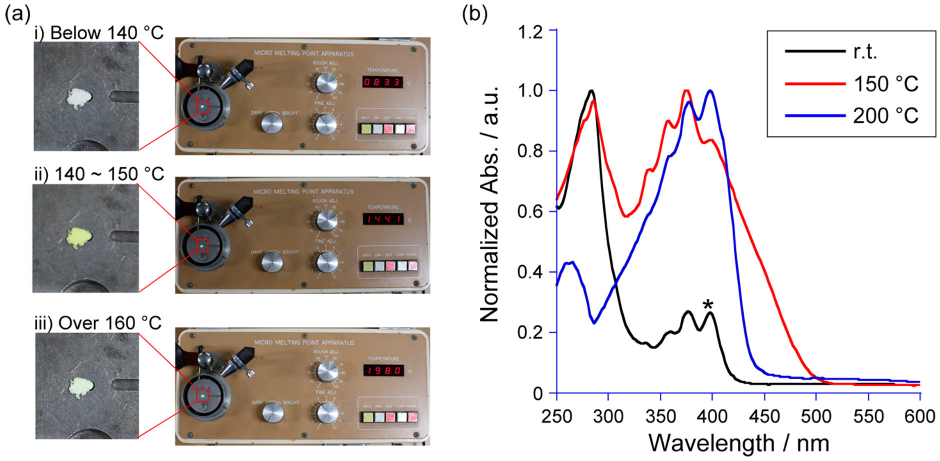


Figure 7. (a) Temperature-dependent color changing of **1**′: (i) below 140 °C, (ii) 140−150 °C, (iii) over 160 °C. (b) Solid-state UV−vis spectra (KBr pellet) of **1**′ at room temperature (r.t., black line): after heating at 150 °C (red line) and after heating at 200 °C (blue line). Asterisk marked absorbance on r.t. at the 400 nm, attributed from anthracene unit, indicates a C−C bond dissociation of **1**′ to **1** occurred for a small amount of **1**′ by pressing during the KBr pellet preparation.

peaks, and from the proton hyperfine coupling constants (a_H), the radical spin is mainly delocalized on two anthracene units but slightly leaking into a benzene ring (Figure S12).

Next, the C−C bond dissociation of **1**′ was investigated. A measurement of differential scanning calorimetry (DSC) in solid state showed that the C−C bond dissociation gradually occurred over 130 °C, and two exothermic peaks at 146 and 155 °C were observed (Figure 6a). The experimental value of the energy difference (ΔH_{iso}) between **1** and **1**′ is estimated to be 22.8 kcal mol^{-1}, which is greater than those between the anthracene and anthracene dimer (15.6 kcal mol^{-1}), and bi(anthracene-9,10-dimethylene) (**BAD**) and its photoisomer, (8.4−9.3 kcal mol^{-1}) (Figure 6b)[5b,17] because the one-side tethering of two anthracenes by the rigid benzene ring causes a high strain energy when a photoisomerization occurred.

Although the reason why two exothermic peaks were observed in DSC measurement is unclear,[18] one possibility is that a solid-state phase transition caused by structural changing from **1**′ to **1** may occur, resulting in an endothermal process. Another possibility is that stepwise C−C bond dissociation may occur during the isomerization because the distances of C9 to C9′ and C10 to C10′ in both **1** and **1**′ are largely different

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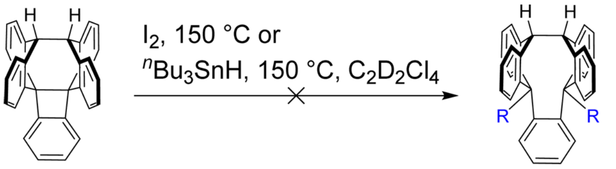
(Scheme 2).[9c,18] In theoretical study, Kertesz and co-workers recently reported that the stepwise dissociation of **BAD** photoisomer to **BAD** via diradical intermediate is energetically favored, compared with a concerted dissociation pathway,[19] even though the C−C bond lengths at C9 to C9′ and C10 to C10′ in **BAD** and **BAD** photoisomer are almost the same. In fact, upon heating the **1′**, a color change from colorless to yellow starting around 140−150 °C could be observed, and a color fading from yellow to colorless over 160 °C, affording **1**, was also confirmed (Figure 7a).[20] A solid-state UV−vis spectra using KBr pellet method (Figure 7b) and heating **1′** at 150 °C showed a broad shoulder absorbance (red line) reaching at 500 nm, which is not observed in both **1** (black line) and **1′**(blue line) and indicates an intermediate existing in the C−C bond dissociation process.[21] However, no direct evidence of the intermediate was obtained by ESR and variable-temperature (VT) Raman measurement; a silent ESR spectrum and no significant peak shifts in VT Raman spectra (Figure S13). Hence, to trap the dissociation intermediate, several reactions such as solid-state heating of **1′** with I_2 at 150 °C in a vacuum-sealed tube or treating **1′** with $n\mathrm{Bu_3SnH}$ in solution at 150 °C were attempted, but unfortunately no trapping of the intermediate to afford **3a-b** (R = I or H) and normal isomerization from **1′** to **1** was confirmed (Scheme 3).

Scheme 3. Attempts To Trap the Isomerization Intermediate of 1′



1'

3 (R = I or H)

Finally, due to having a long C−C bond exceeding 1.68 Å in **1′**, mechanical dissociation of the long C−C bond[22] by simple grinding was performed because several radical σ-dimers with a long C−C bond are known to show the C−C bond dissociation by a mechanical grinding.[23] In addition, **BAD** photoisomer is known to show a C−C bond dissociation with mild energy by a pressure-catalyzed system.[24] By grinding a white powder of **1′**, no distinct difference of solid-state emission between before and after grinding of **1′** was confirmed, but a yellow emission dissolving in chloroform could be observed, whereas no emission in chloroform was observed from before ground **1′** (Figure 8).

After grinding for 30 min, ^{1}H NMR was measured and showed an existence of **1**, indicating the mechanical C−C bond dissociation of **1′** occurred (Figures S14−18). The conversion yield from **1′** to **1** was qualitatively estimated as 6% by the integration ratio between **1** and **1′**.[25] On the other hand, no C−C bond dissociations in anthracene photodimer were observed by ^{1}H NMR. Then, by embedding a large strain in anthracene photodimer derivatives, the activation energy in the C−C bond dissociations reduced, and they can be a good candidate for mechanical stimuli responsible materials.

■ CONCLUSION

We have synthesized and investigated 1,2-di(9-anthryl)benzene **1** and its photoisomer **1′** as a fundamental moiety of anthracene-based π-cluster molecules. Both structures are unambiguously confirmed by ^{1}H NMR and X-ray crystallography. Intramolecular anthracene−anthracene interaction of **1** is evaluated by UV−vis, fluorescence spectra, and CV measurements. Moreover, in the radical cation state of **1**, a charge delocalization between anthracene units is also observed by oxidative UV−vis-NIR titration and ESR measurements. By photoisomerization of **1** to **1′**, a high strain energy of 22.8 kcal mol^{-1} can be stored, and **1′** has a long C−C bond that can be dissociated by simple mechanical grinding. To our best knowledge, this is the first example of C−C bond dissociations in anthracene photodimer derivatives using a manual grinding method. Further investigations of the C−C bond dissociation process of **1′** to **1** and the anthracene-based π-clusters such as cyclic and radial systems with more than two anthracene units are ongoing in our laboratory.

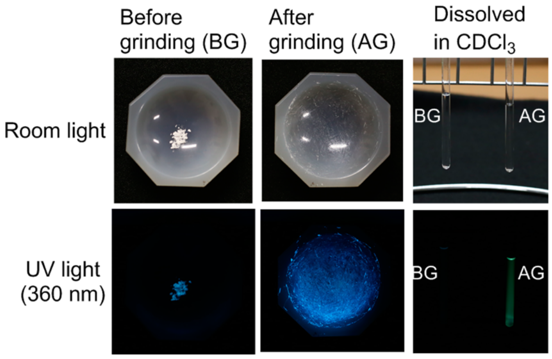


Figure 8. Photo images of before (BG) and after (AG) mechanical grinding of **1′** under room light and UV light (360 nm) as well as an emission difference between BG and AG in $CDCl_3$ solution.

■ EXPERIMENTAL SECTION

General. All experiments were performed under nitrogen atmosphere. Toluene and ethanol were used after distillation from calcium hydride and magnesium, respectively. Anhydrous dichloromethane was purchased and used without further purification for reactions. For measurements, dried dichloromethane was prepared by distillation with calcium hydride. Column chromatography was performed with silica gel. Analytical thin-layer chromatography (TLC) was performed on a glass plate coated with silica gel (0.25 mm thickness) containing a fluorescent indicator. ^{1}H and ^{13}C NMR spectra were recorded, and chemical shift values are given with respect to internal tetramethylsilane for ^{1}H NMR (δ 0.00) and $CDCl_3$ for ^{13}C NMR (δ 77.0). Data collection for X-ray crystal analysis was performed on Imaging Plate (Mo-Kα, λ = 0.71069 Å). The structure was solved with direct methods and refined with full-matrix least-squares. Cyclic voltammetric measurement was recorded with a glassy carbon working electrode and a Pt counter electrode in dichloromethane containing 0.1 M $n\mathrm{Bu_4NPF_6}$ as a supporting electrolyte. The experiment employed an Ag/$AgNO_3$ reference electrode and was done under argon atmosphere at room temperature. The UV−vis spectra were recorded in dichloromethane. The solid-state UV−vis spectra were recorded using integral sphere unit. The emission spectra were recorded in dichloromethane. The emission quantum yield were recorded using fluorescence integral sphere unit. The ESR spectrum was recorded in dichloromethane.

Computational Methods. All DFT calculations were performed with the Gaussian 03 program. The molecular geometries were optimized with a C_2 (for **1**), C_{2v} symmetry (for **1′**), or C_2 (for radical cation state of **1**) constraint at the B3LYP/6-31G** (for **1** and **1′**) or at the UB3LYP/6-31G** (for radical cation state of **1**) level of calculation. TD calculations of radical cation state of **1** were performed with the same geometry constraints by a UB3LYP/6-31G** method.

Synthesis of 1,2-Di(9-anthryl)benzene ***1***. 9-Anthracenylboronic acid[26] (2.22g, 10 mmol), *ortho*-diiodobenzene (1.00 g, 3.0 mmol), $Pd(PPh_3)_4$ (693 mg, 0.60 mmol), and K_2CO_3 (2.50 g, 18 mmol) were dissolved in toluene (30 mL), ethanol (5 mL), and water (5 mL) under nitrogen atmosphere. After stirring the reaction mixture for 12 h at 110 °C, the reaction was quenched with water. Organic layer was extracted with dichloromethane and washed with brine. After removal of the solvent in vacuo, the crude material was subjected to column chromatography on silica gel (hexane → hexane: dichloromethane = 10:1 to 1:1) to afford the title compound **1** (414 mg, 0.96 mmol, 32%) as colorless to pale yellow solid. Mp: >300 °C. MS (EI): m/z 430 [M^+]. ^1H NMR (500 MHz, $CDCl_3$): δ 7.92 (s, 2H), 7.83 (dd, J = 1.0 Hz, J = 8.5 Hz, 4H), 7.79 (s, 4H), 7.59 (d, J = 8.5 Hz, 4H), 7.13 (m, 4H), 6.98 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.8, 135.4, 133.5, 130.6, 129.7, 127.8, 127.6, 127.4, 126.1, 124.4, 124.2. Anal. calcd for $C_{34}H_{22}$: C, 94.85; H, 5.15. Found: C, 94.66; H, 5.04.

Synthesis of Photoisomer ***1′***. A precipitate of **1** (150 mg, 0.35 mmol) in dichloromethane (50 mL) was stirred with photoirradiation (365 nm, using LED lump) until the green-yellow emission of **1** disappeared. After removal of the solvent in vacuo, the crude material was subjected to column chromatography on silica gel (hexane:dichloromethane = 4:1) to afford the title compound **1′** (144 mg, 0.33 mmol, 96%) as white solid. Mp: 140−160 °C (isomerization to **1** in solid state). MS (EI): m/z 430 [M^+]. ^1H NMR (500 MHz, $CDCl_3$): δ 7.73 (m, 2H), 7.67 (m, 2H), 7.01 (dd, J = 1.0 Hz, J = 7.5 Hz, 4H), 6.84 (td, J = 1.5 Hz, J = 7.0 Hz, 4H), 6.80−6.76 (m, 8H), 4.64 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.5, 142.3, 142.2, 128.9, 127.4, 126.8, 125.8, 125.4, 124.3, 73. 5, 53.1. Anal. calcd for $C_{34}H_{22}$: C, 94.85; H, 5.15. Found: C, 94.65; H, 5.13.

Crystal Data for ***1***. Monoclinic, space group $C2$ (no. 5), a = 16.3261(13) Å, b = 8.3889(3) Å, c = 11.0680(5) Å, β = 132.380(9)°, V = 1119.75(11) Å^3, T = 200 K, Z = 2, R_1 (wR_2) = 0.0322 (0.0977) for 154 parameters and 2216 unique reflections. GOF = 1.090. CCDC 1430987.

Crystal Data for ***1′*** *(C_3H_7NO)*. Monoclinic, space group $P2_1/n$ (no. 14), a = 10.4067(4) Å, b = 16.6913(5) Å, c = 15.6434(6) Å, β = 90.2612(9)°, V = 2717.25(17) Å^3, T = 200 K, Z = 4, R_1 (wR_2) = 0.0625 (0.1510) for 352 parameters and 6173 unique reflections. GOF = 1.047. CCDC 1430988.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications Web site. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00134.

Characterization of data for all new compounds and crystallographic data (ZIP)

Experimental methods and data (PDF)

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Notes

The authors declare no competing financial interest.

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